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INCINERATOR OPERATING PARAMETERS WHICH CORRELATE WITH PERFORMANCE

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Overall results indicate that CO levels have only a tenuous relationship with DE and vary somewhat with the compound being burned; CO varies significantly with excess air and other combustion parameters. The highest levels of PICs and unburned POHCs (Principal Organic Hazardous Constituents) occurred at high CO levels. For at least three of the compounds tested, the above results were apparently related to thermal quenching of combustion reactions as evidenced by the 100°C drop in exhaust gas temperature that resulted from increasing excess air from the lowest to the highest levels.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes the results of an initial evaluation of carbon monoxide (CO) as an indicator of incinerator performance under conditions of non-optimal excess air level and excessive post-flame heat removal.

For further information, please contact the Alternative Technologies Division/Thermal Destruction Branch of the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser, Director
Hazardous Waste Engineering Research Laboratory

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Overall results indicate that CO levels have only a tenuous relationship with DE and vary somewhat with the compound being burned; CO varies significantly with excess air and other combustion parameters. The highest levels of PICs and unburned POHCs (Principal Organic Hazardous Constituents) occurred at high CO levels. For at least three of the compounds tested, the above results were apparently related to thermal quenching of combustion reactions as evidenced by the 100°C drop in exhaust gas temperature that resulted from increasing excess air from the lowest to the highest levels.

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INCINERATOR OPERATING PARAMETERS WHICH CORRELATE WITH PERFORMANCE

INTRODUCTION

The Resource Conservation and Recovery Act requires that incinerator operators destroy the toxic substances they burn. Compliance with this requirement is usually determined in a trial burn in which the incinerator operator must demonstrate that a Destruction and Removal Efficiency (DRE) of 99.99% can be achieved for designated toxic substances known as Principal Organic Hazardous Constituents (POHCs) in a representative waste stream. It is assumed that, if the incinerator can destroy the designated POHCs, it can also destroy the other toxic substances present in the waste. The operating conditions used during the trial burn, combined with the emissions data from the trial burn stack sampling, are used to set the operating limits in the incinerator's permit.

There are several problems with the permitting process outlined above. First, the trial burn data only indicate how well the incinerator was operating during the time that the data were being taken, typically only a period of a few days. No information is obtained on how the incinerator might respond if fuel, or especially waste, conditions change. Waste streams vary widely in composition and one incinerator may burn many different toxic substances over its useful life, resulting in unavoidable and frequent changes in waste feed conditions. It is difficult to generalize the results of a trial burn to predict how the composition of the incinerator exhaust will change under these varying conditions.

A method is needed to continuously monitor incinerator exhaust and to warn an operator of the onset of performance deterioration (where performance might be measured in terms of decreased POHC DRE or increased penetration of total emissions of potentially toxic compounds). A considerable amount of research currently underway has concentrated on monitoring some component in the exhaust gas stream, either a commonly occurring exhaust component such as carbon monoxide (CO), total unburned hydrocarbons (THC) or some difficult-to-burn tracer spiked into the waste feed.

The experiments discussed in this report were focussed on determining whether or not certain operating parameters of an incinerator correlate with performance and hence might be used to monitor performance. The general approach for these experiments initially involved varying the types and relative amounts of reactants (i.e., fuel/POHC and oxygen) and subsequently varying the degree to which the reactants were mixed. The results of these preliminary studies are reported here to suggest further avenues of research.

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Two sets of experiments are discussed in this report. In the first set, CO level, POHC destruction and PIC (Products of Incomplete Combustion) formation were observed as a function of excess air and (secondarily) post-flame temperature. In the second set, CO and fuel/POHC destruction were observed as a function of change in Swirl Number (a measure of the angular momentum imparted to the combustion air) and nozzle position.

DESCRIPTION OF EXPERIMENTAL EQUIPMENT

A Turbulent Flame Reactor (TFR), constructed under EPA contract number 68-02-3633 and subsequently modified at the EPA's Center Hill Laboratories, was the experimental combustor used (see Figure 1). Fuel and POHC (simulated waste) were delivered to the TFR under nitrogen pressure from three one-gallon fuel tanks. The fuel/POHC mixture entered the TFR at the bottom of the reactor through a 60° spray angle, hollow-cone, pressure-atomizing nozzle (Delavan Manufacturing Co., West DesMoines, IA, nominal flowrate of 1.0 gph of water at 125 psig). Actual cold-flow flowrates of the heptane fuel (generally 0.5 gph) were measured by timing its collection in a graduated cylinder. Combustion air, supplied by an air compressor, entered the TFR through an International Flame Research Foundation (IFRF) adjustable swirl windbox. Gears on the bottom of the windbox allowed the Swirl Number to be adjusted from 0 to 2.76. A single-pass, cooling water jacket removed much of the heat generated by the TFR flame and quenched most of the post-flame reactions. Further thermal decomposition of POHCs escaping the flame was thereby minimized, thus the concentrations of PICs are expected to be maximized. Operation of the TFR was designed to emphasize flame destruction efficiency (DE).

Exhaust gases were sampled at the exit port of the TFR. Three sampling probes were used: one for DE determination via sorbent trap sampling; one for the continuous monitoring of carbon monoxide (CO), carbon dioxide (CO_2), and oxygen (O_2); and one for continuous total unburned hydrocarbon (THC) measurement. Volatile POHCs and PICs were collected on sorbent tubes filled with Tenax-GC® resin. The sampling system used is shown in Figure 2. Exhaust gases were removed from the exit port of the TFR and passed through a heated length of 1/4 inch (outside) diameter teflon tubing kept at approximately 130°C. The heated portion of the sample line ended six inches upstream of the Tenax-filled sorbent tube in order to allow the sample gases to air-cool from 130°C to about 24°C (or less) while passing through a particulate filter. In the first set of tests, the exhaust gases then passed through a sorbent tube packed with 1.5 grams of Tenax-GC® resin, a diaphragm pump, a rotameter and a dry gas meter and were finally exhausted to the atmosphere. The sorbent trap samples collected in this way were thermally desorbed and analyzed by a gas chromatograph (GC) equipped with a Hall Detector. In the second set of tests, 0.25 grams of resin were used and a gas chromatograph/mass spectrometer was used for the analyses.

Figure 3 shows a diagram of the continuous monitoring system used. As mentioned earlier, a single probe collected sample gas for CO, CO_2 and O_2 analyses. Sample gases drawn through the probe passed through a particulate filter, a silica-gel gas drier and a diaphragm pump before being split and

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TURBULENT FLAME REACTOR

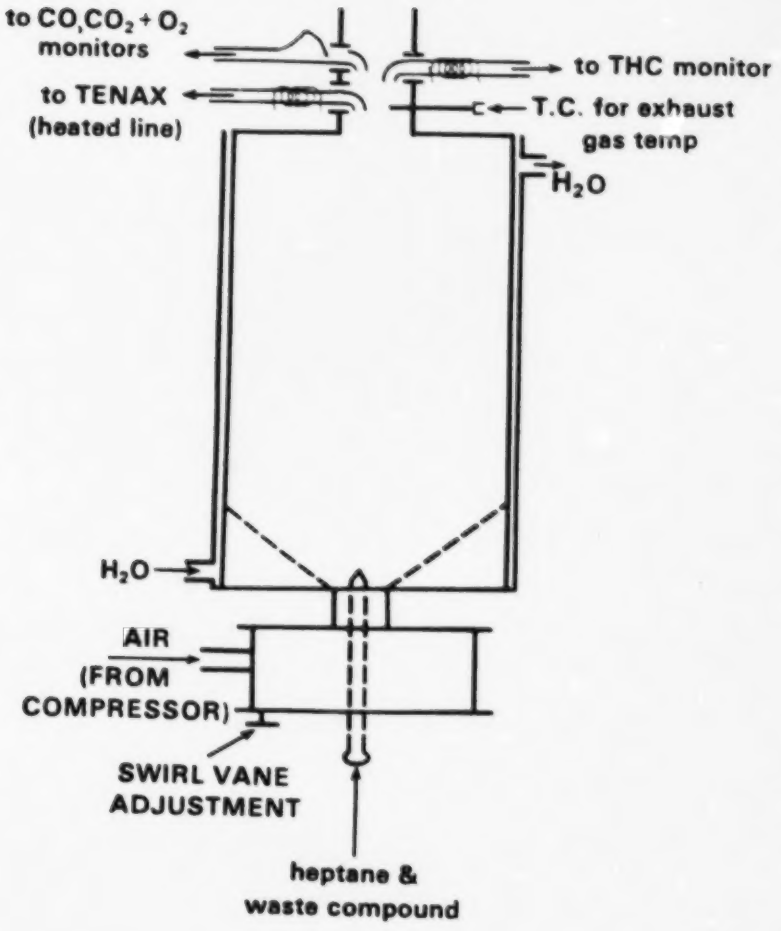

Figure 1. Turbulent Flame Reactor (TFR).

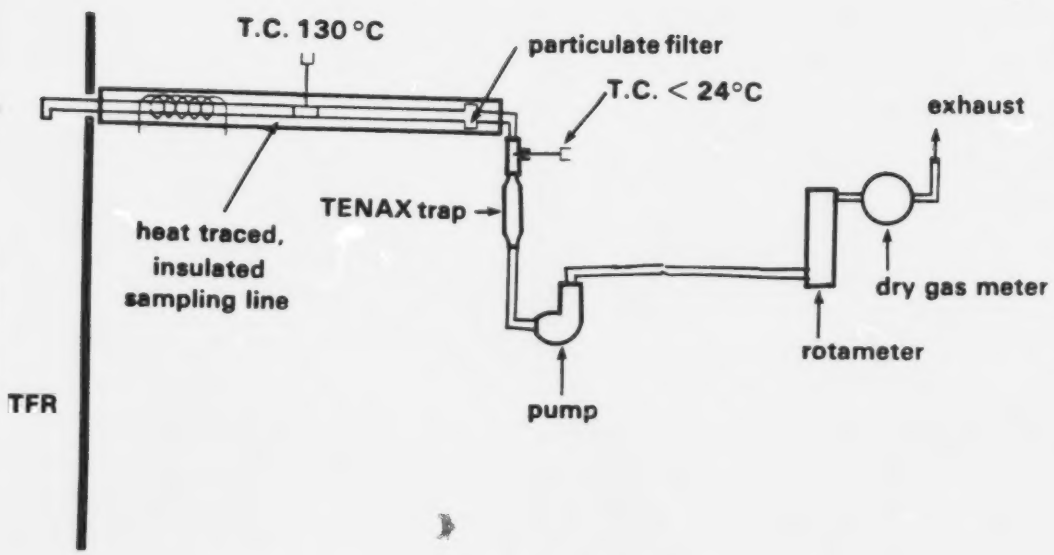

Figure 2. Tenax Sampling Train.

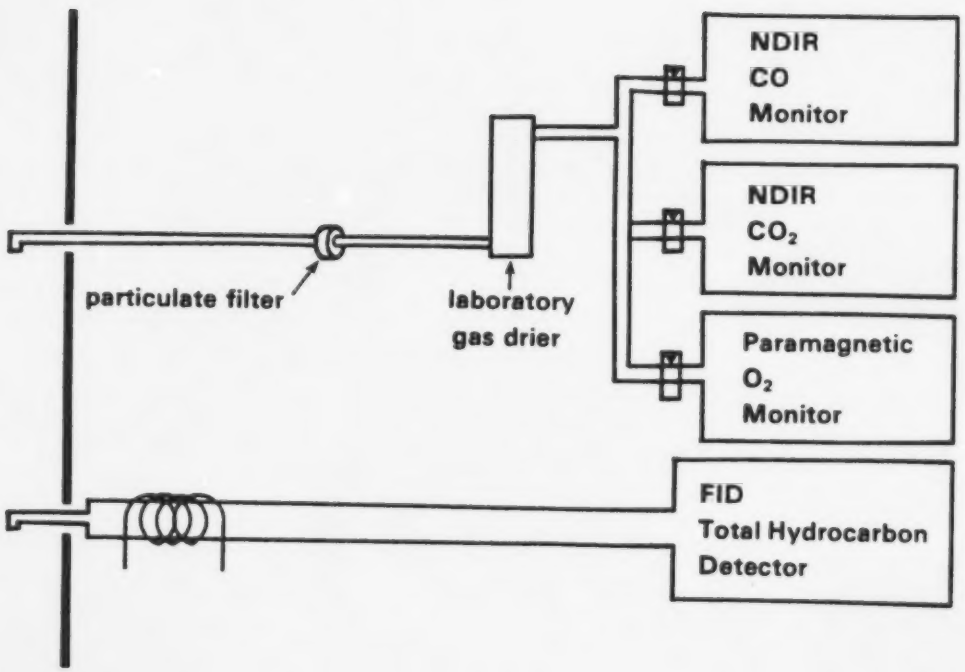

Figure 3. Continuous Monitors.

sent to each of the three monitors. Sample gas for the hydrocarbon analyzer was collected through a separate heated sample line kept at 130°C. Beckman Model 865 and 864 non-dispersive infra-red analyzers were used to detect both CO and CO_2 respectively. A Beckman paramagnetic monitor Model 755 was used to detect O_2. THC measurements were made with a Beckman 402 hydrocarbon analyzer (flame ionization detector).

Exhaust gas temperature was measured using a Type K (chromel-alumel) thermocouple located at the exit port of the TFR in close proximity to the other sampling lines.

DESCRIPTION OF EXPERIMENTAL WORK

To determine changes in POHC destruction and PIC formation with changes in the types of POHCs burned, a two-mole percent mixture of either 1,1,2-trichloroethylene (TCE), 1,1,2,2-tetrachloroethane (TCA), carbon tetrachloride (CCl_4), chlorobenzene (C_6H_5Cl, CLBZ), or 1,1,2-trichloro-1,2,2-trifluoroethane ($C_2Cl_3F_3$, Freon-113, F113) in 98 percent heptane was burned in the TFR. During each of these five tests, the excess air level was varied from 120% of theoretical air to 230% of theoretical air. This spanned the limits of flame stability and produced a wide range of CO levels. The bulk of the data obtained emphasized the fuel-lean side of stoichiometric conditions (i.e., excess air number greater than unity or equivalence ratio less than unity). At five, or sometimes six, sets of operating conditions, Tenax trap samples were drawn to determine levels of POHC destruction and PIC formation. To test mixture effects, a sixth test was conducted in which both chlorobenzene and Freon-113 were burned in heptane under conditions similar to those used in the first five tests (i.e., two mole percent of each). The GC/Hall was set up to detect only a limited number of PICs; they were: TCE, CCl_4, TCA, CLBZ, chloromethane, methylene chloride and chloroform.

At one set of operating conditions during each test, the flame was deliberately extinguished by shutting off the flow of fuel to the TFR two minutes into a five-minute sampling run while an actual exhaust sample was being taken. Sampling continued for the remaining three minutes in order to determine what levels of PICs and unburned POHCs were emitted during this simulated "upset" condition.

To investigate the effect of nozzle position and swirl on CO concentration in the exhaust and, to a limited extent, on POHC destruction and PIC formation, a series of tests was conducted in which the nozzle position and Swirl Number were varied while burning heptane at otherwise "optimum" stoichiometry as determined by the earlier series of tests. Swirl was varied from 0.62 to 2.39 which represented the limits of flame stability.

RESULTS AND DISCUSSION

Variation of Excess Air Level: Effect on CO Emission and Exhaust Temperature.

Variation of excess air level was accomplished at constant fuel flowrate by varying the air flowrate. In doing so, atomization quality was held constant, but intensity of turbulent mixing was changed although Swirl Number was held constant at 0.86. The effect of increasing air flow-rate on CO emission and exhaust gas temperature are shown in Figures 4 and 5, respectively, for all periods when Tenax resin samples were drawn. Theoretical air is plotted in percent (%TA) on the abscissa and either CO (ppm corrected to 0% O_2) or exhaust gas temperature (degrees Celsius) on the ordinate. CO emission exhibited a minimum and rose sharply below a percentage theoretical air of about 135 to 140% and more gradually above about 160%. These observations are comparable with an earlier study by Kramlich et. al. (1) carried out in a nearly identically configured combustor. The dependence of CO emission on %TA for values of %TA less than about 135% can be explained as resulting from poor mixing. Although the overall stoichiometry remained fuel lean, i.e., %TA greater than 100%, pockets of fuel rich gas were probably present which resulted in the formation of CO as a thermodynamically metastable product. At %TA values greater than about 160%, temperature effects probably contributed to the increased emission of CO as will be discussed in more detail below. CO emissions did not appear to be a strong function of the POHC burned at the two-mole percent level of POHC used in this study. [A note should be made with respect to each of the Figures in this Report that illustrate data resulting from this study: first, if a solid line or lines have been drawn, that means that they represent the best least-squares fit of the regressions performed; second, if dashed lines have been drawn, that means that the authors are suggesting the type of relationship that may have existed; and third, if no lines have been drawn, the reader is free to draw his own conclusions.]

As anticipated, exhaust temperature decreased monotonically with increasing %TA over the range tested (%TA > 120%). It should be noted that an energy balance performed on the TFR indicated that the major path for removal of heat was through the cooling water (approximately 45,000 Btu/hr) and that increasing %TA from 149% to 199% increased the heat leaving with the flue gases only marginally (from about 15,000 to 18,000 Btu/hr). Nevertheless, CO emission clearly increased over that range of %TA and exhibited a clear dependence upon exhaust temperature as shown in Figure 6. The dependence of CO emission on temperature under oxygen-rich conditions can be taken as qualitative evidence for thermal quenching by the additional air. Under conditions of excess air, it is currently accepted that the pathway for oxidation of CO involves the hydroxyl radical (2). In turn, hydroxyl radical has a large activation energy which results in a very strong concentration dependence upon temperature, in turn effecting a strong temperature dependence on the rate of CO oxidation. Thus, localized cooling of the flame region resulting from the rapid mixing of fuel with an excess of combustion air might plausibly be expected to lead to poor DE and the formation of stable intermediate compounds such as CO and other PICs, even though the major route of heat loss was through the water-cooled walls of the TFR.

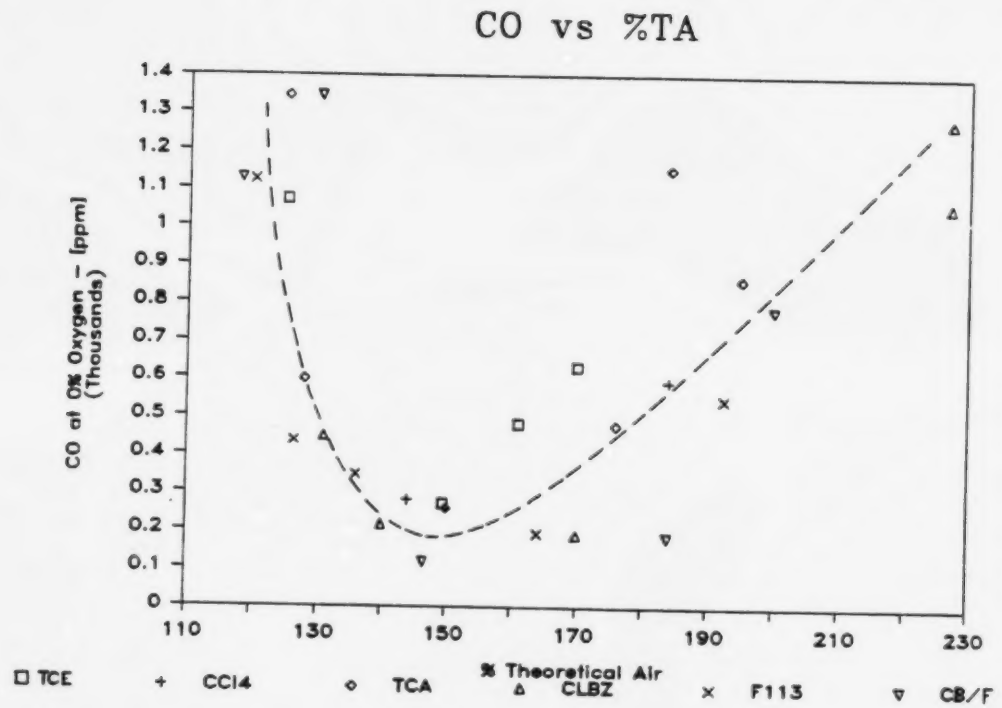

Figure 4. CO vs. % Theoretical Air (%TA): All Compounds.

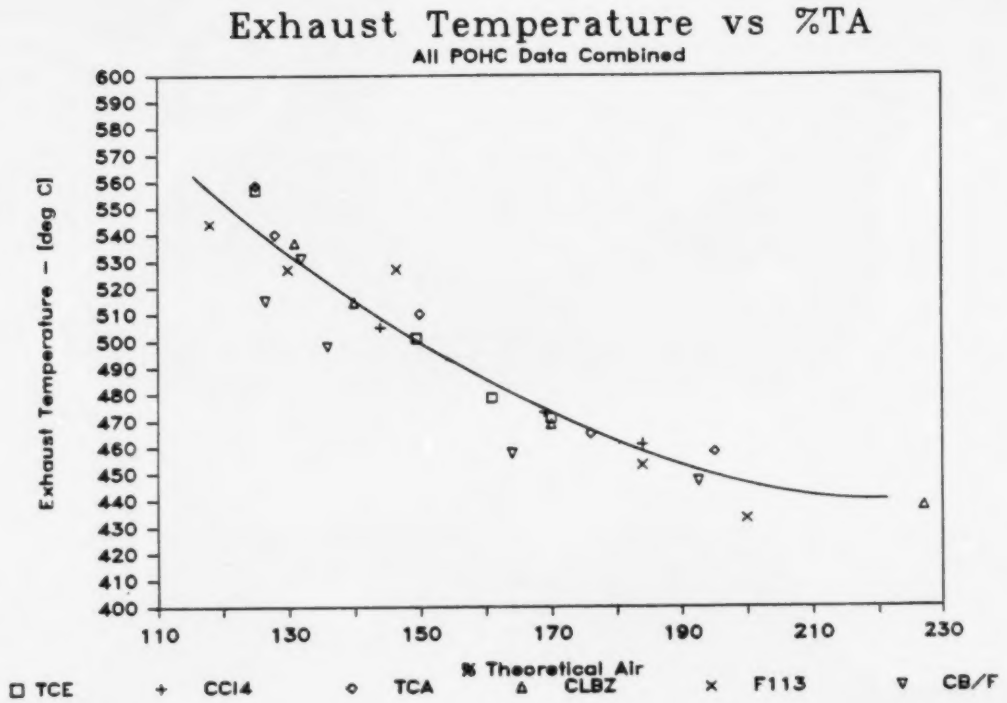

Figure 5. Exhaust Temperature vs. %TA.

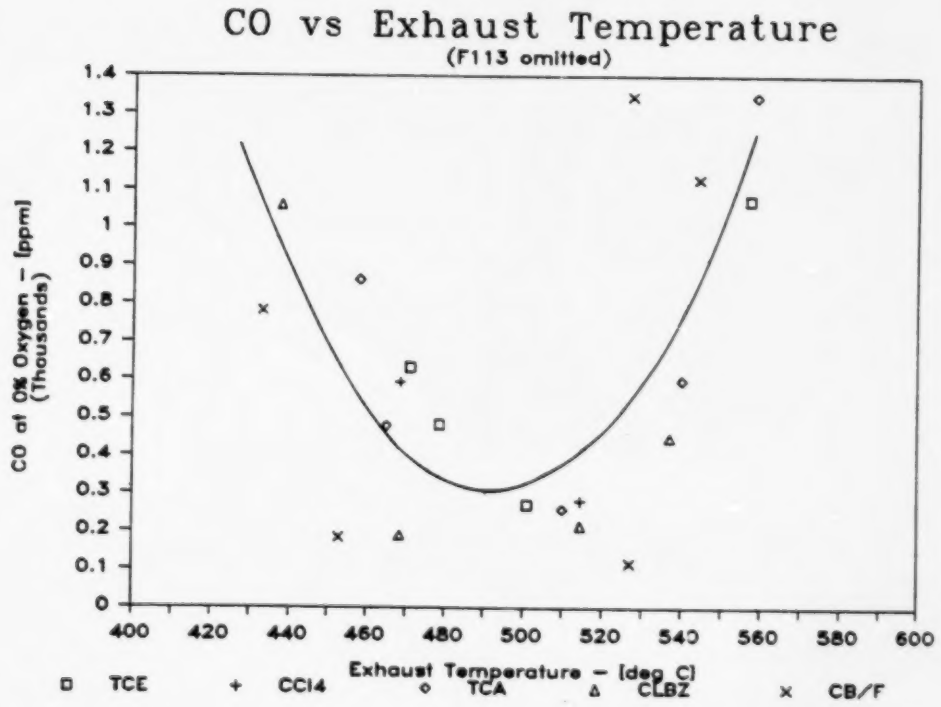

Figure 6. CO vs. Exhaust Temperature.

Variation of Excess Air Level: Effect on POHC DE and PIC Formation.

Effect on POHC DE

The POHC DE or "penetration" (Pt = 1-DE) data are presented as a function of %TA in Figures 7 through 11. Figure 7 displays all data combined, while Figures 8 through 11 separate out the data in such a way as to better display trends for individual POHCs. Figure 8 represents the Pt or DE for TCE, CLBZ and CCl_4 for %TA greater than 130%; Figure 9 the penetration or DE of TCA for %TA greater than 130%; Figure 10 the penetration or DE of Freon-113 over the entire range of %TA tested, and Figure 11 the penetration data from the combined mixture of chlorobenzene and Freon-113 in heptane over the entire range of %TA tested. Logarithmic axes are used to present POHC penetration or DE because the data points span several orders of magnitude. Points plotted as $Log_{10}(Pt)= -6$ or DE = 99.9999% represent a situation where the amount collected on the Tenax trap was below detection limits (detection limits, of course, varied with the compound being burned). Points marked "F.O." represent a sample drawn during the simulated flame-out failure condition.

With the exception of the Freon-113 test, the data exhibit a trend of increasing POHC penetration with increasing excess air for %TA greater than about 130%, the point which corresponds to the approximate location of the minimum in CO emission. The POHCs TCE, CLBZ and CCl_4, more-or-less appear to lie in a common band (Figure 8), while the penetration of the POHC TCA is about an order of magnitude lower. In terms of difficulty of incinerability, this ordering would be consistent with the data on gas-phase thermal stability under oxidizing conditions reported by Dellinger et al. (3) for $T_{99}(2)$ (i.e., the temperature at which 99% of the material decomposes at 2 seconds residence time). The $T_{99}(2)$ for TCE, CCl_4, CLBZ and TCA were reported as 913, 824, 810 and 601°C respectively.

The DE data are consistent with the hypothesis that some of the fuel/POHC mixture may have escaped the flame and was subsequently thermally decomposed. The relatively close $T_{99}(2)$'s of TCE, CCl_4 and CLBZ do not permit a clear distinction in order of incinerability, i.e., these compounds might have experienced a temperature history that rapidly brought them below the $T_{99}(2)$ required for rapid decomposition. However, TCA's much lower $T_{99}(2)$ would have permitted its continued thermal decomposition in the TFR whose average residence time under these conditions would be on the order of a few seconds. Wolbach and Garman (4) have tentatively concluded on the basis of pilot-scale testing with and without water-cooled walls that the in-flame DE contributed only 90 to 99% of the total DE observed in their study and that the remainder resulted from post-flame reaction.

The behavior of Freon-113 appeared to be anomalous (Figure 10). When burned individually, it did not appear to exhibit a consistent trend with increasing excess air. A possible explanation for the anomalous behavior would be that the particular analytical procedure utilized during this series of tests (GC/Hall Detector) could not distinguish between chloroform and Freon-113. As will be discussed later, chloroform was a common PIC and therefore, residual concentrations of Freon-113 could be

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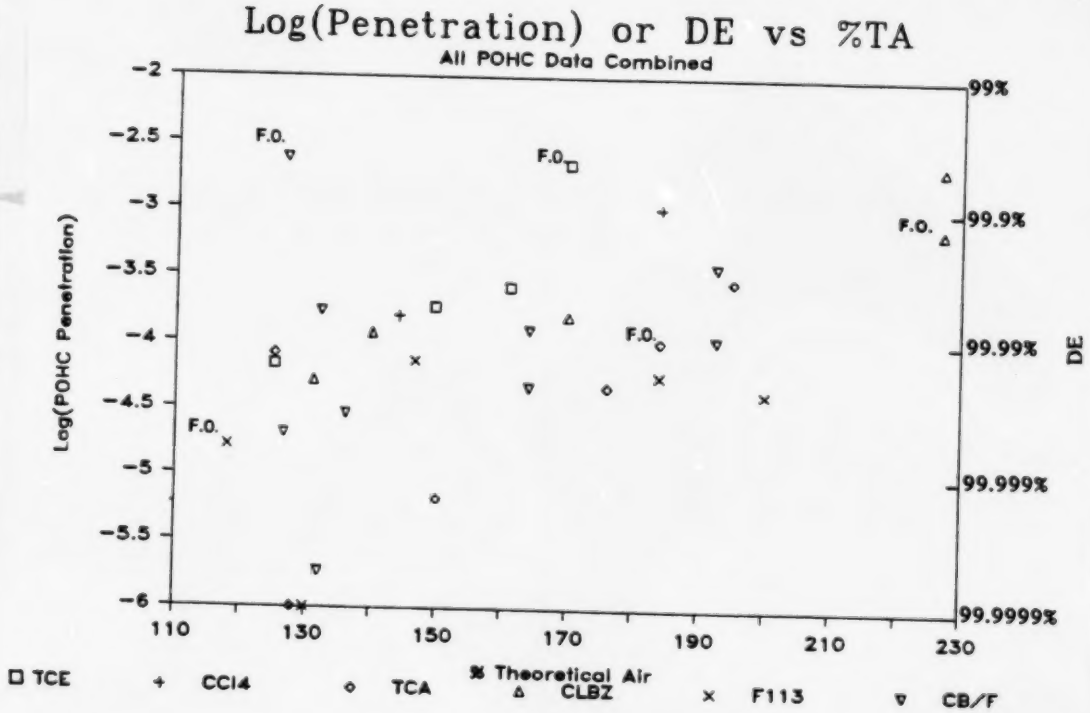

Figure 7. POHC Penetration or DE vs. %TA: All Compounds.

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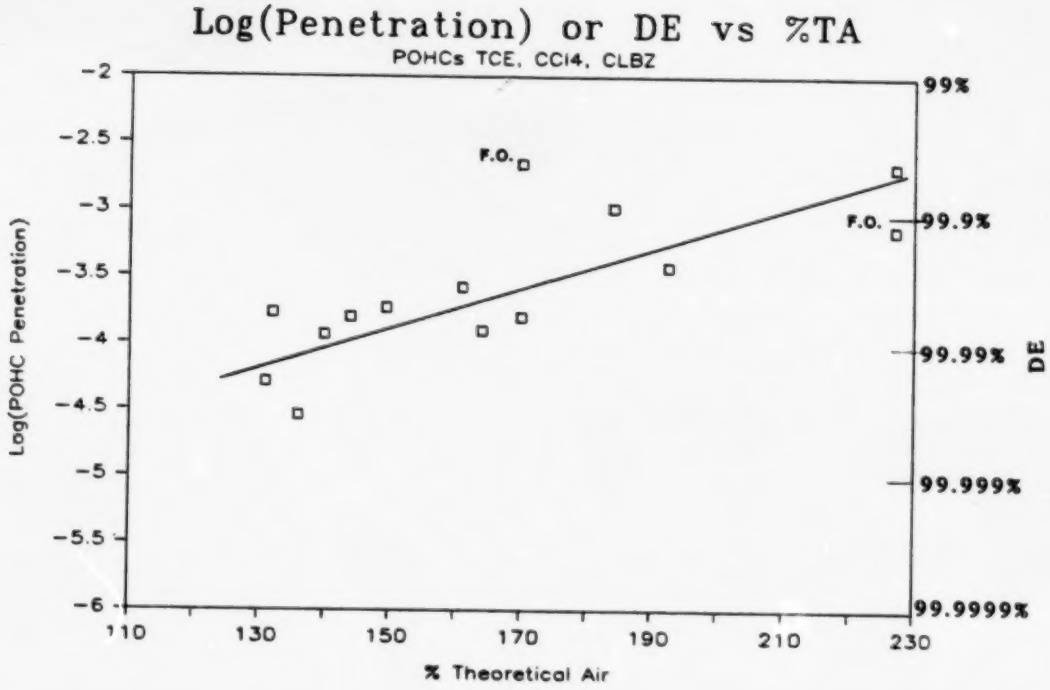

Figure 8. POHC Penetration or DE vs. %TA (for TCE, CCl_4 and CLBZ).

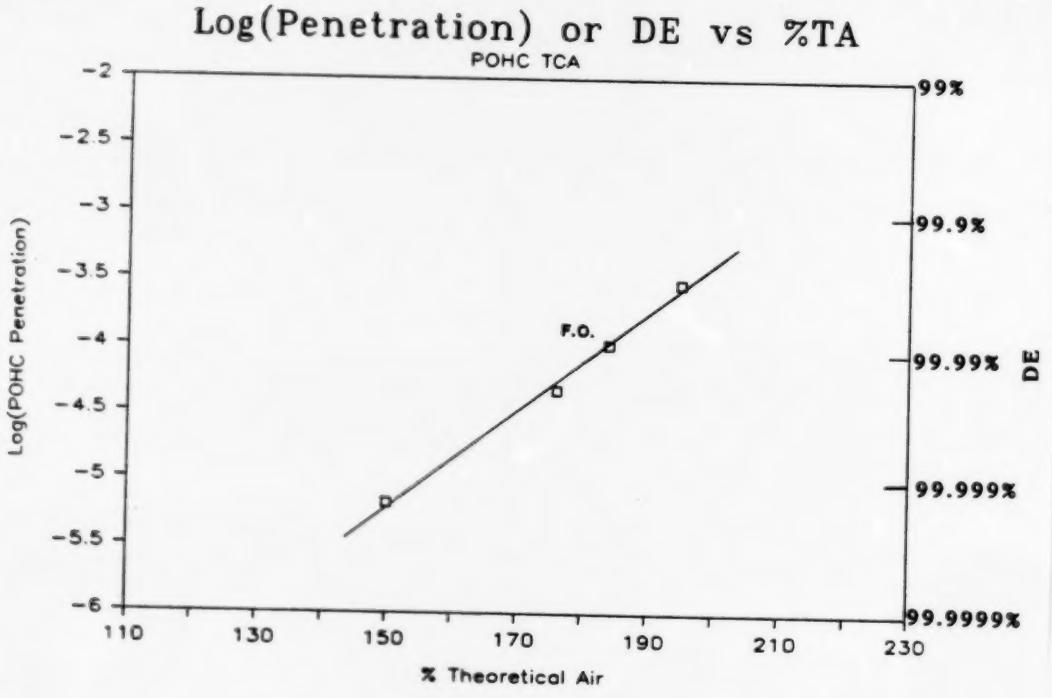

Figure 9. POHC Penetration or DE vs. %TA (for TCA).

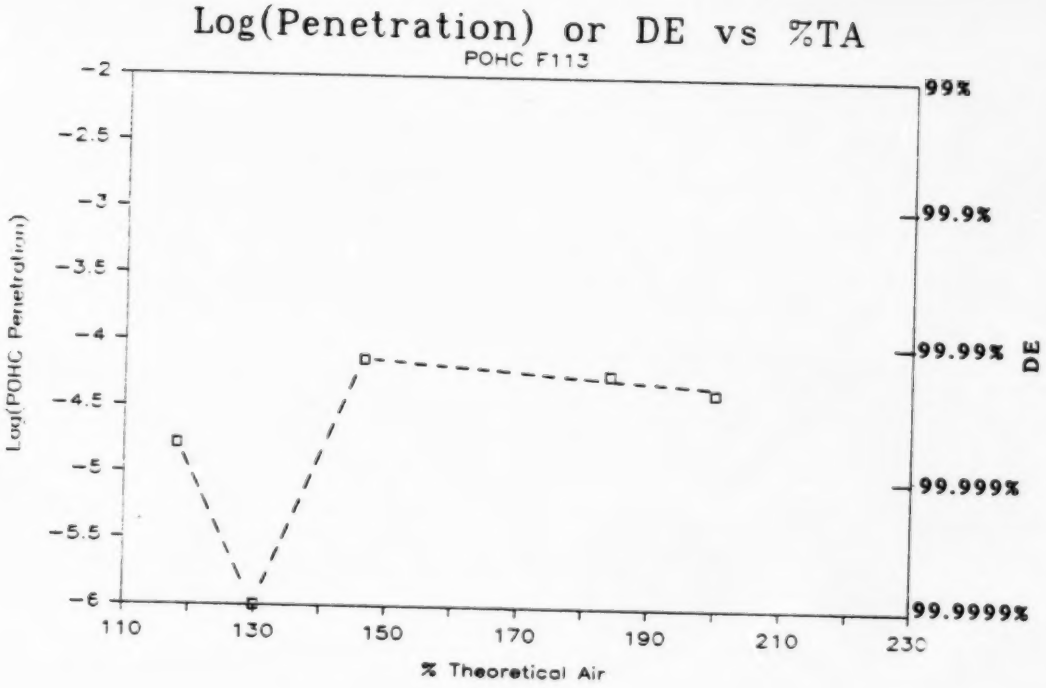

Figure 10. POHC Penetration or DE vs. %TA (for Freon-113, F113).

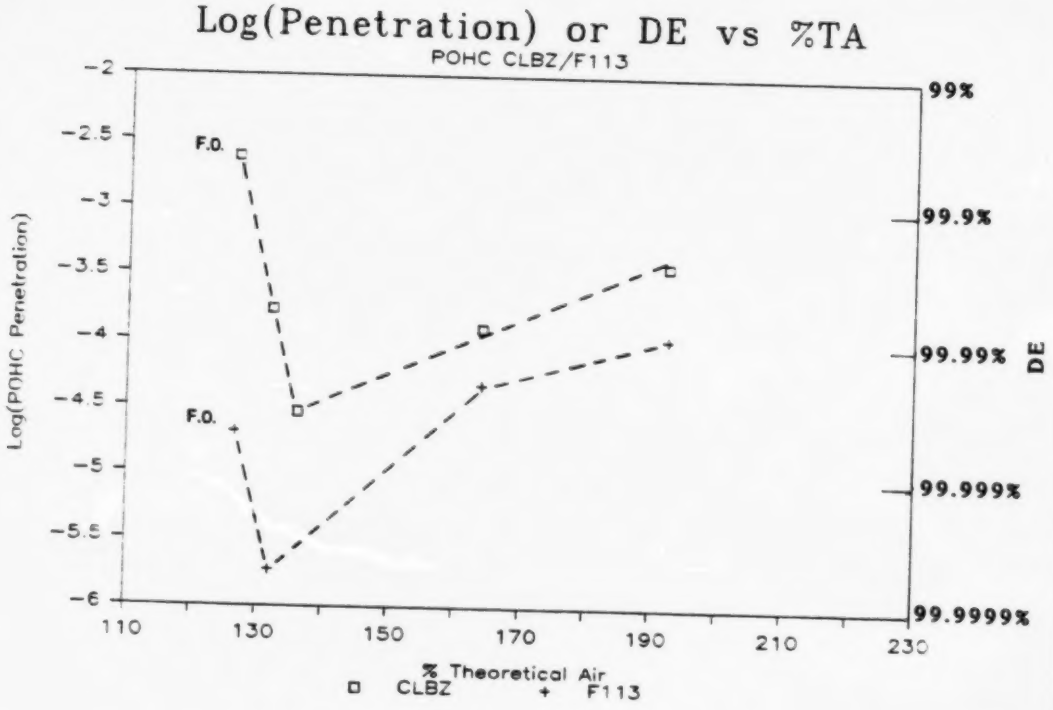

Figure 11. POHC Penetration or DE vs. %TA (for CLBZ/F113).

confused with chloroform that was formed as a PIC. When Freon-113 was burned with CLBZ, its emissions increased with %TA (above about 135% TA) as did those for chlorobenzene. The comparative ease of destruction of Freon-113 would be consistent with the observations reported by Dellinger et al. (3) that Freon-113 was relatively fragile. It is possible that chloroform was formed as a PIC from each compound. Further study of Freon-113 with an improved analytical methodology would be needed to resolve the apparently inconsistent data observations.

The relationship between CO and POHC DE was explored as shown in Figures 12, 13 and 14. Figure 12 displays all the data for the individual POHC tests for %TA in excess of 130%. Figure 13 shows only the data for TCE, CLBZ and CCl_4 for %TA in excess of 130%. Figure 14 presents the data from the TCA test. A trend of increasing POHC penetration with increasing CO emission is evident from the plots, though with a greater amount of scatter in the data compared with increasing excess air. The reason for selecting only those data obtained for %TA greater than 130% was to avoid the multiple-valued nature of the CO versus %TA curve. A linear correlation between CO emission and the logarithm of POHC penetration cannot be expected over the entire range of %TA. The reader is cautioned that even when examining only the data on the high excess air limb of the CO curve, a linear appearance of the relationship between CO and the logarithm of penetration is probably either fortuitous or an artifact of using a logarithmic scale. Nevertheless, the trend is distinct and gives rise to the suggestion that a positive correlation between CO and POHC Pt was present for the high excess air limb conditions tested.

POHC DE at low excess air did not appear to increase as rapidly as would be expected from the same CO level corresponding to high excess air conditions, though a few data points were obtained which are suggestive of increased POHC penetration (see Figure 7 and 11). As discussed earlier, this may simply reflect a situation where CO would be a thermodynamically metastable product in the locally fuel-rich environment of a fuel droplet. In a fuel-rich environment, hydroxyl radical concentration would be relatively low, and slower oxidation of CO would be expected. Subsequent cooling of average gas temperature by the waterwall could have reduced temperatures sufficiently that, by the time oxygen was mixed into the fuel-rich pocket, the CO had become "frozen in." On the other hand, POHC destruction could have been effected by other flame radicals such as H atom or simple thermal decomposition (5). Such conjecture is purely speculative at this point, nevertheless it points out a need for additional study of the effects of low excess air on the flame destruction of chlorinated POHCs.

As shown earlier in Figure 5, a monotonically decreasing correlation between exhaust gas temperature and excess air existed over the range of conditions tested. Therefore, it is not surprising that POHC DE could be related to TFR exhaust temperature. Figures 15, 16 and 17 illustrate POHC emissions normalized by total mass of exhaust gas versus exhaust gas temperature plotted on an arithmetic scale. Note the slight multiple-valued nature of POHC emissions evident at high exhaust temperature corresponding to %TA less than 130%. A monotonic trend of POHC Pt is shown in Figure 18

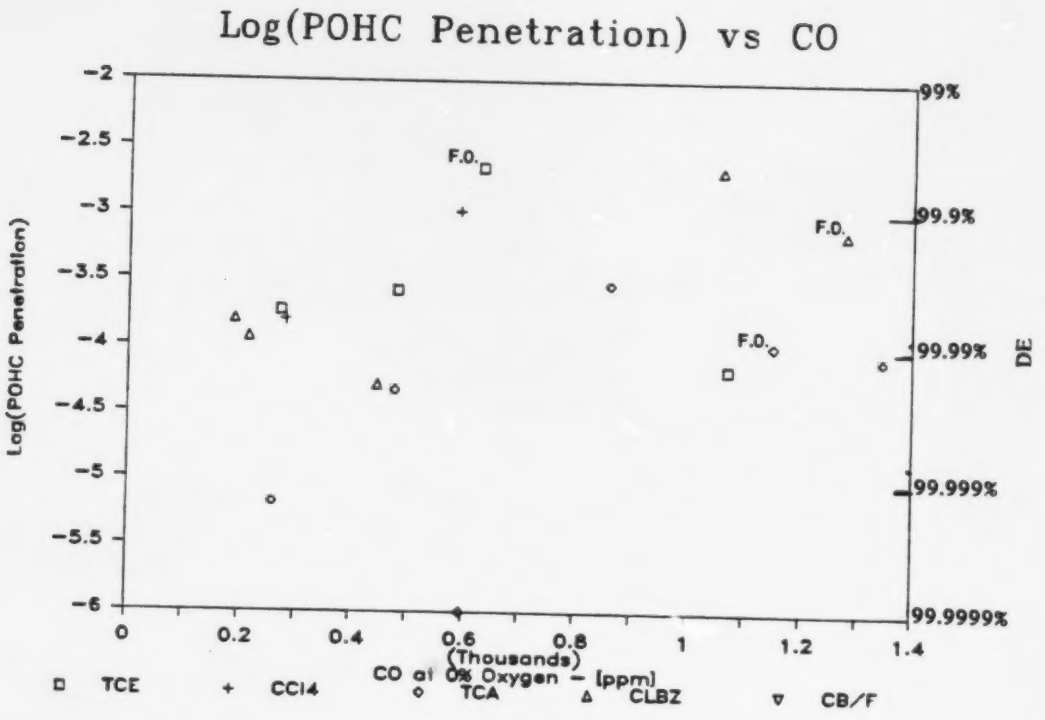

Figure 12. POHC Penetration or DE vs. CO (for All Compounds).

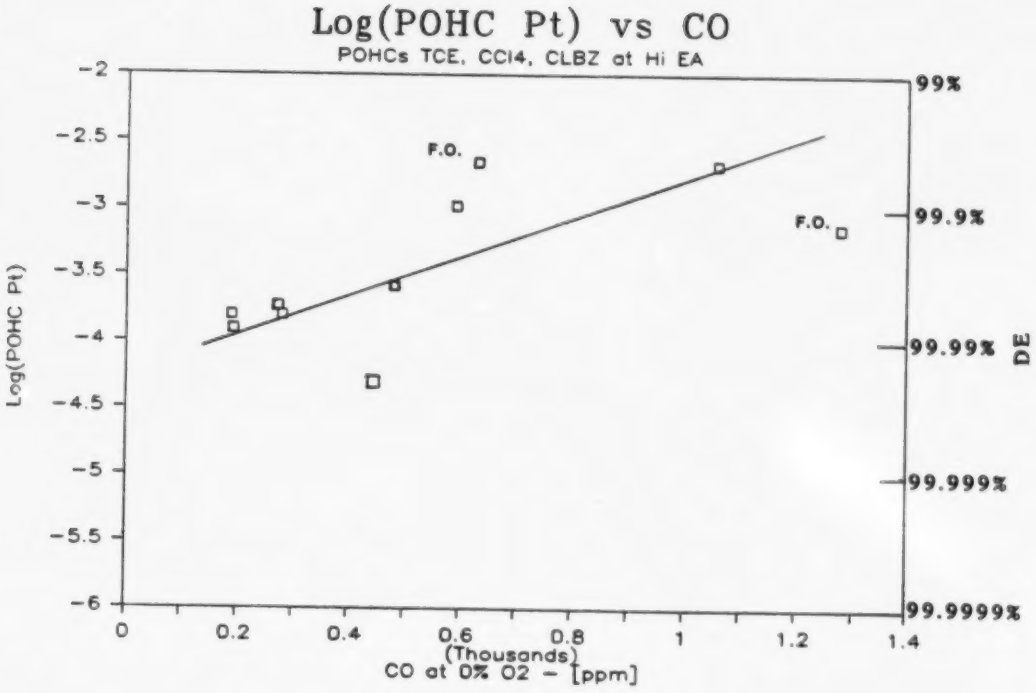

Figure 13. POHC Penetration vs. CO (for TCE, CCl_4 and CLBZ).

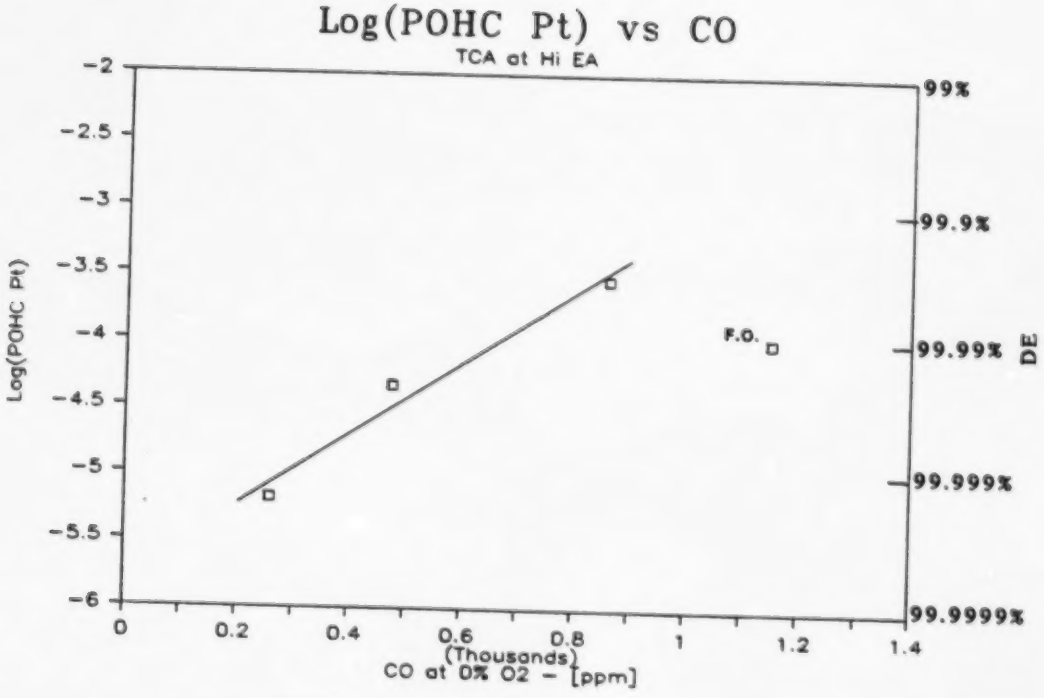

Figure 14. POHC Penetration vs. CO (for TCA).

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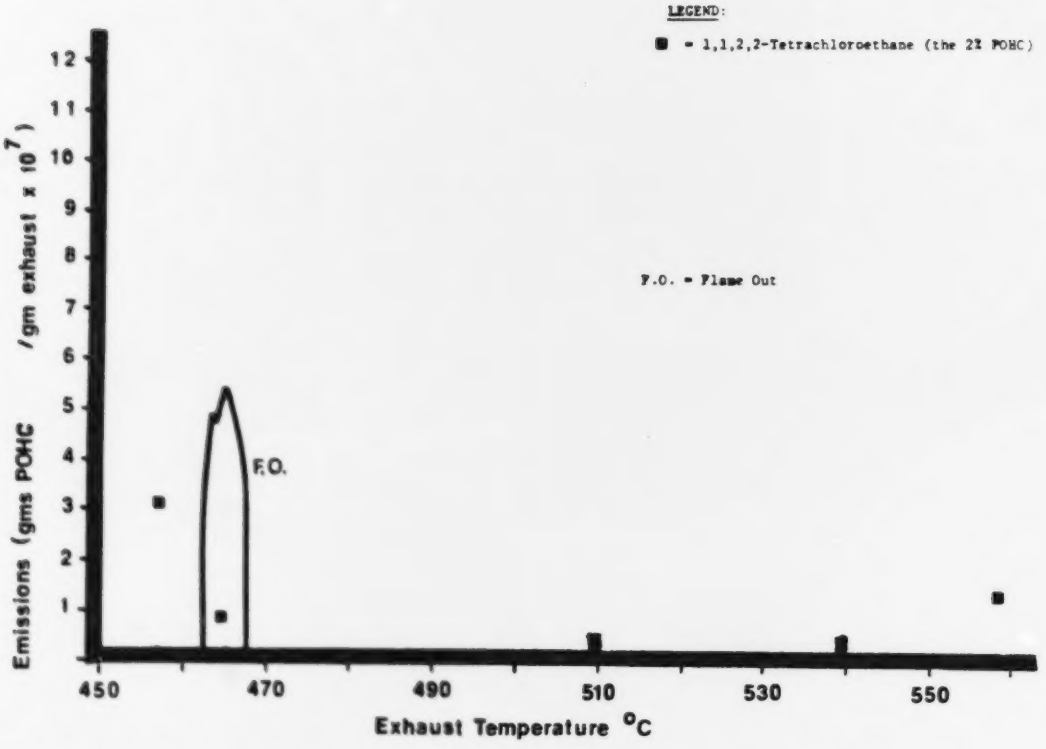

Figure 15. POHC Emissions vs. Exhaust Temperature for the TCA Burn.

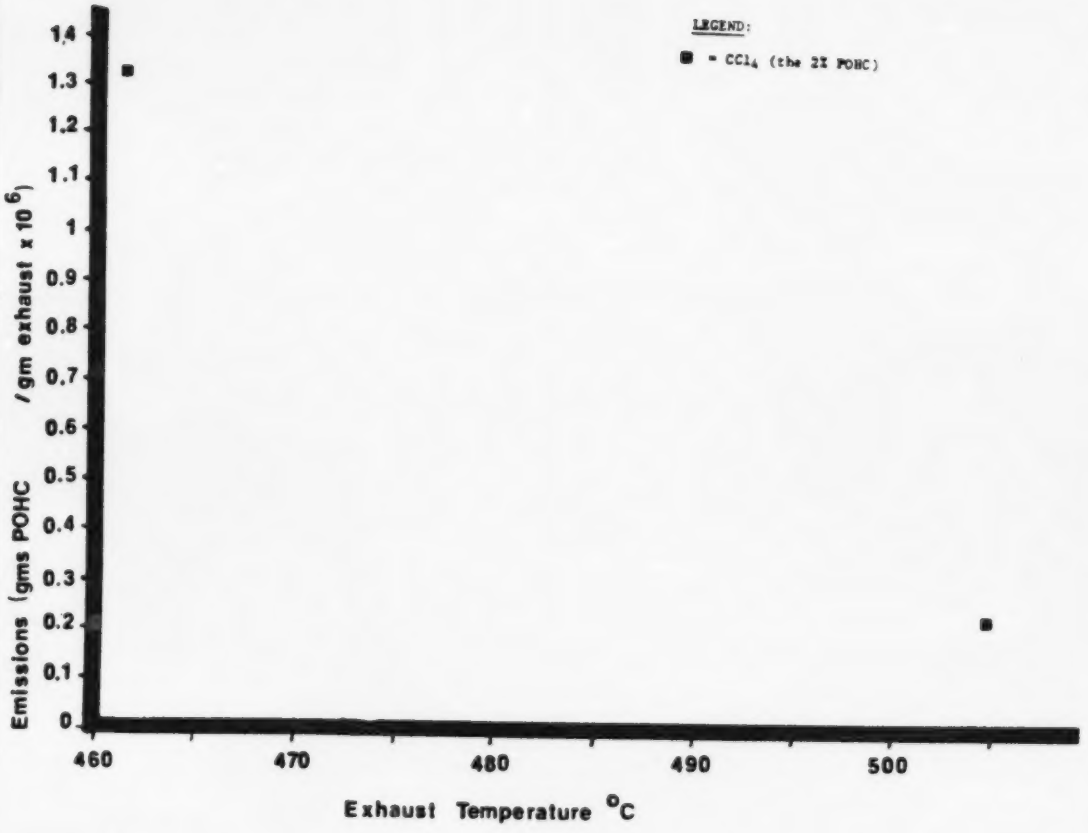

Figure 16. POHC Emissions vs. Exhaust Temperature for the CCl_4 Burn.

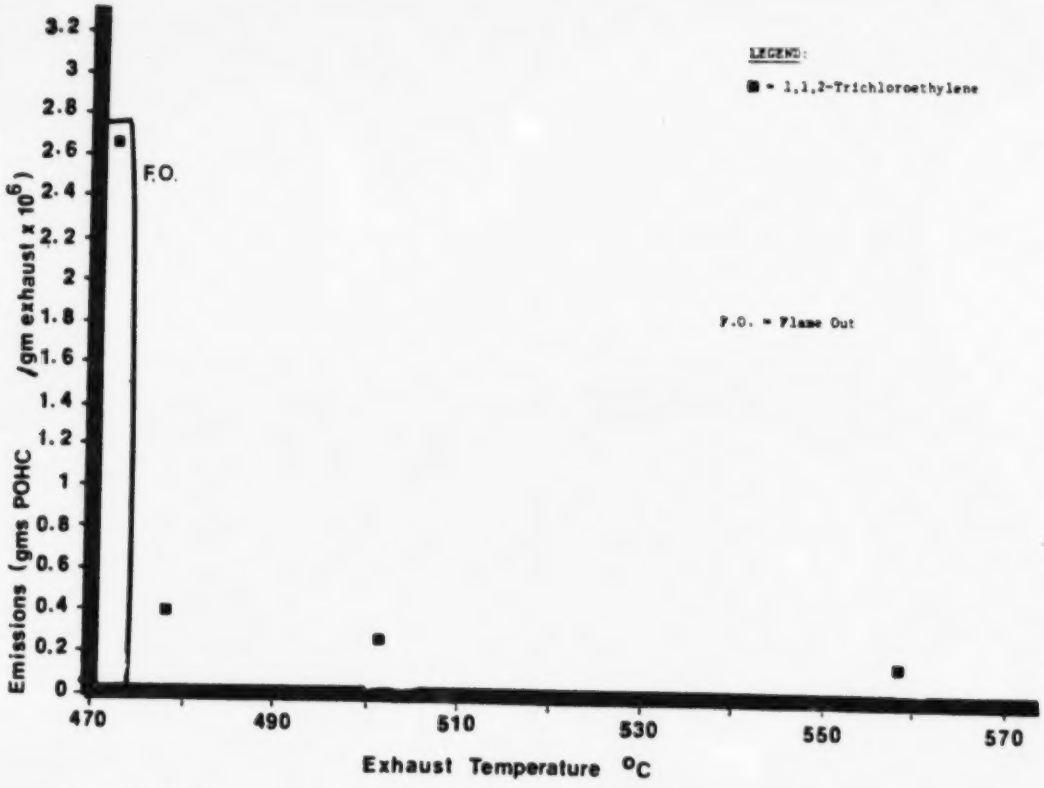

Figure 17. POHC Emissions vs. Exhaust Temperature for the TCE Burn.

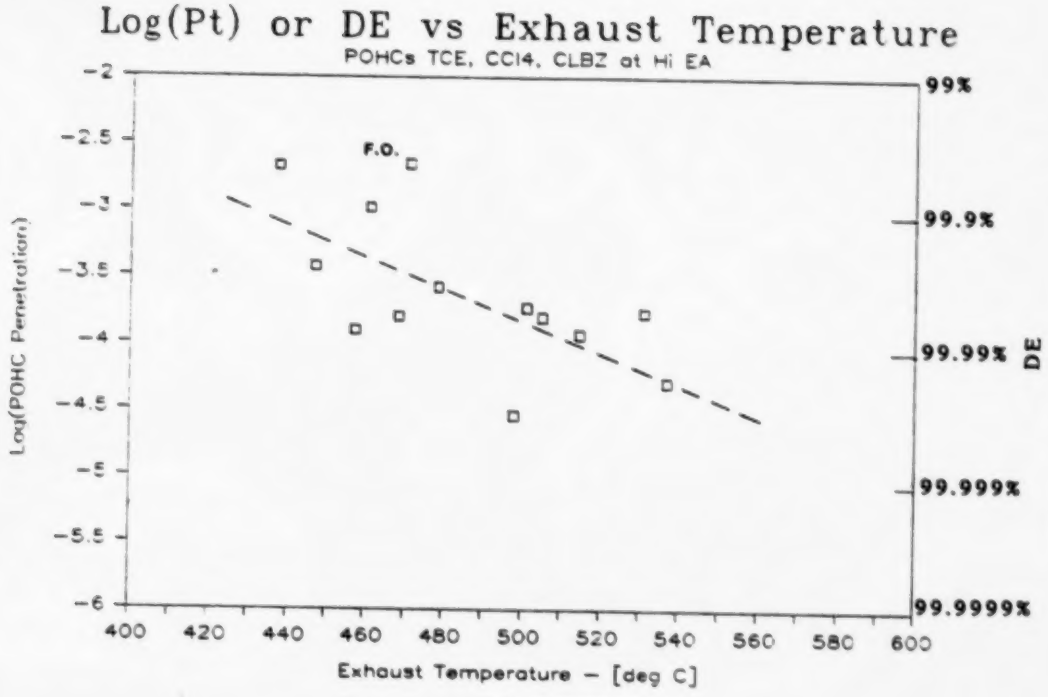

Figure 18. POHC Penetration or DE vs. Exhaust Temperature (for TCE, CCl_4 and CLBZ).

for the POHCs TCE, CLBZ and CCl_4 and in Figure 19 for TCA. Again, the degree of scatter is greater with increasing temperature than for increasing excess air, but the tendency is clear.

Effect on PIC Formation

The formation of PICs as a function of excess air provided considerable insight into the chemical transformations occurring in and around the flame zone. These data are shown in Figures 20 through 26. Figure 20 illustrates the relative mass emissions of the POHC TCA and its PICs normalized by the mass of exhaust gas as a function of %TA. The approximate upper and lower bounds of %TA, where CO emissions rose to the levels of 1000 ppm and 500 ppm, are delineated by a vertical line. The normalized mass emission rate of TCA that would correspond to 99.99% DRE is also shown on the Figure as a horizontal line. Note the relative amounts of the PIC TCE in comparison with the POHC TCA emissions. At the extreme value of excess air in this test, the PIC-to-POHC ratio was about 3. This ratio was in a range consistent with that observed by Castaldini (6) in recently reported non-steady-state full-scale boiler tests (PIC-to-POHC ratios from 0.5 to 15). As has been demonstrated now by various groups of investigators, high DE of the POHC does not assure that total emissions of chlorinated organics would meet an equivalent criterion of four nines (i.e., 99.99%) destruction.

The logarithm of the mass fraction, TCE in the exhaust divided by TCA in the feed, is plotted as a function of %TA in Figure 21 in order to better illustrate the relative amounts of the various PICs detected by the analytical methodology applied (Tenax resin and GC/Hall detector). In the discussion of POHC DE, it was mentioned that TCE was presumably more difficult to destroy than TCA. Thus, this experiment conclusively demonstrates that the combustion of a relatively easy to destroy POHC (TCA) can lead to the formation of more difficult to destroy PIC (TCE) particularly in applications where quenching could be a potential mode of DE failure, e.g., boilers. Likely PICs to be formed should be a consideration in the selection of a POHC. The formation of TCE from TCA could have been predicted. Tsang and Shaub (5) pointed out, in the development of the ranking scale that has come to be termed the theoretical flame-mode kinetic(TFMK) ranking, that "complex fragmentation" could provide a "low energy channel for decomposition." They cite as an example, the class of alkyl chlorides, to which 1,1,2,2-tetrachloroethane belongs. The "four center elimination of hydrogen chloride to form the appropriate alkene" (TCE in this case) was set forth as the primary mode of decomposition.

A careful examination of Figure 21 further reveals an interesting phenomenon. As TCE emission increased with increasing %TA, there appears to have been a decrease in CLBZ emission. The same trend may be present in Figure 22, but does not appear as distinctly. One can hypothesize that as chlorine atoms, liberated from the POHC, were "bound up" in other PICs, that the availability of Cl atom to recombine with benzene (a PIC of heptane) was diminished. In other words, the distribution of chlorine atoms among PICs may be a quasi-equilibrium process. Although it is difficult to conceive of an experiment where this could be verified using the TFR system, chemical modeling of the process could prove useful in interpre-

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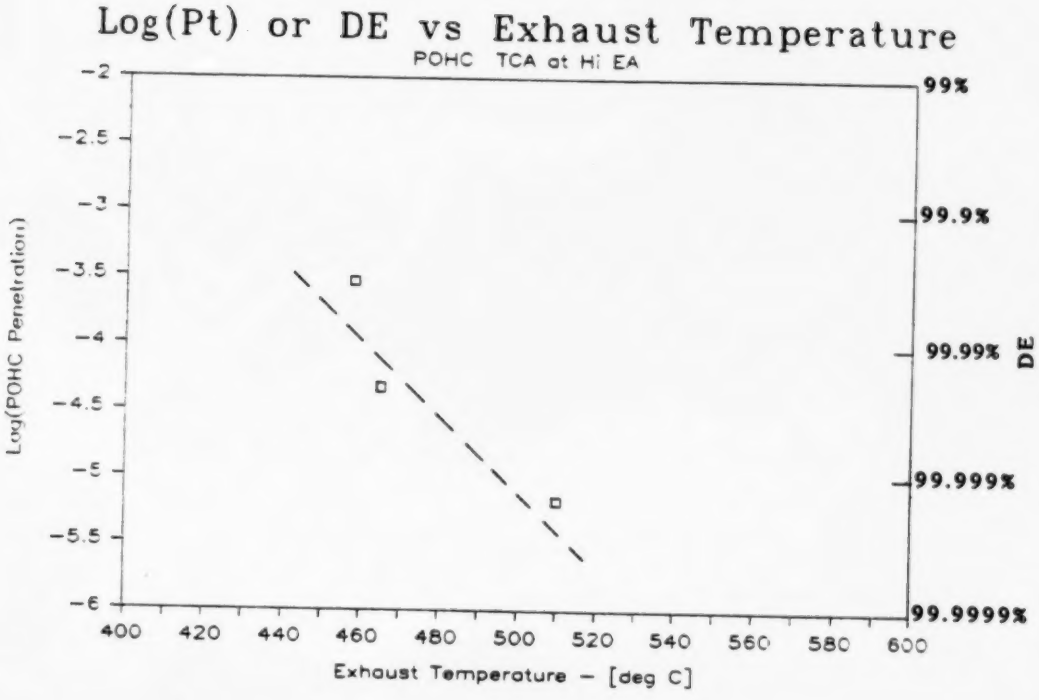

Figure 19. POHC Penetration or DE vs. Exhaust Temperature (for TCA).

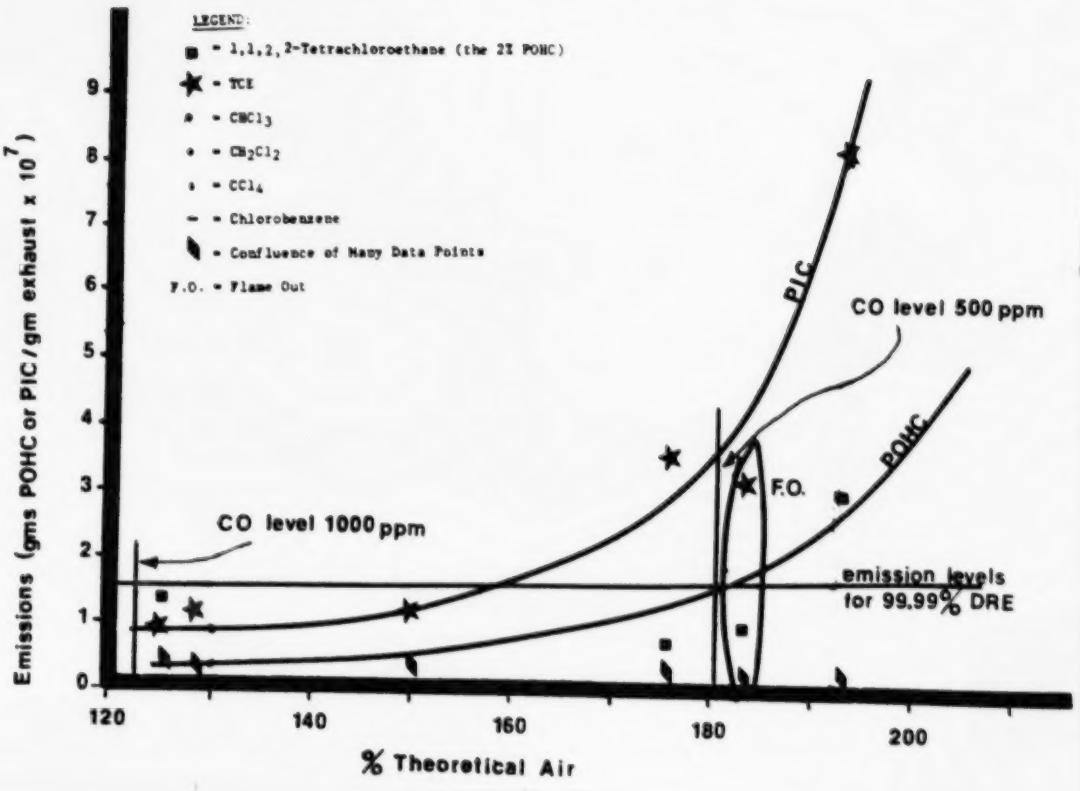

Figure 20. POHC and PIC Emissions for the TCA Burn.

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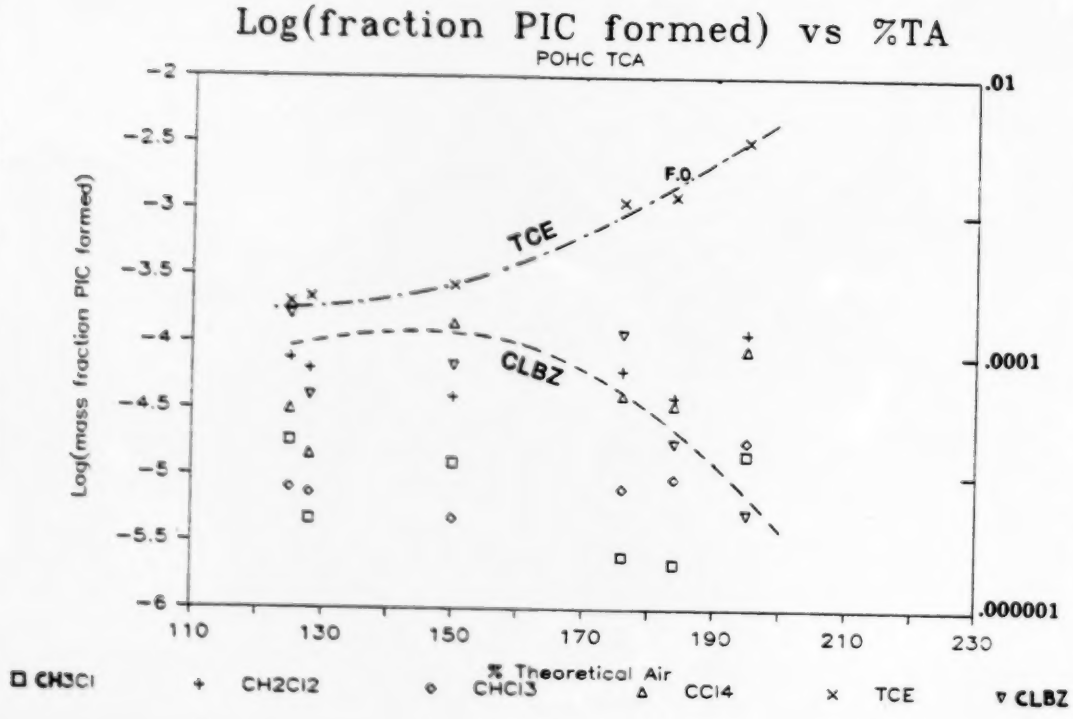

Figure 21. Mass Fraction of PIC Formed vs. %TA (from TCA).

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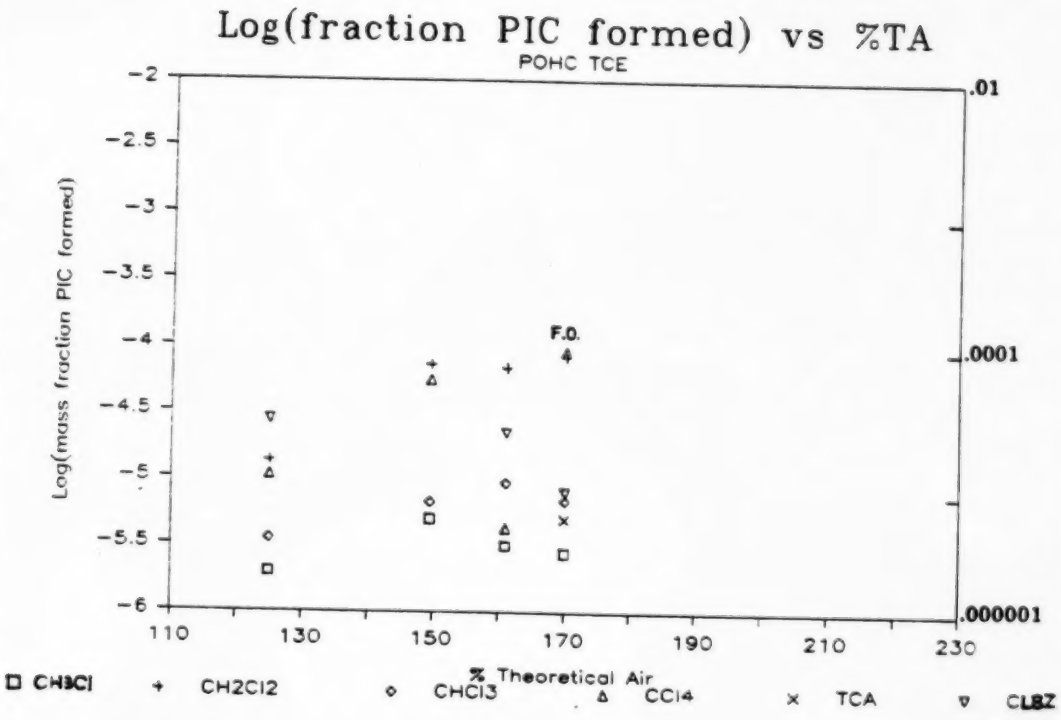

Figure 22. Mass Fraction of PIC formed vs. %TA (from TCE).

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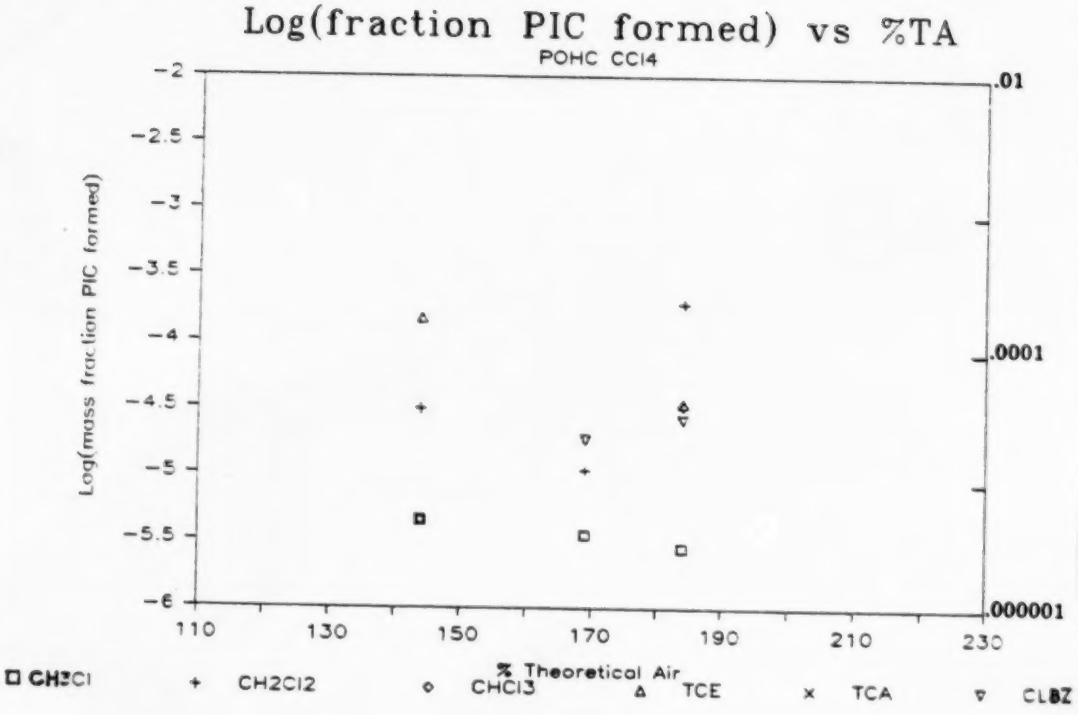

Figure 23. Mass Fraction of PIC Formed vs. %TA (from CCl_4).

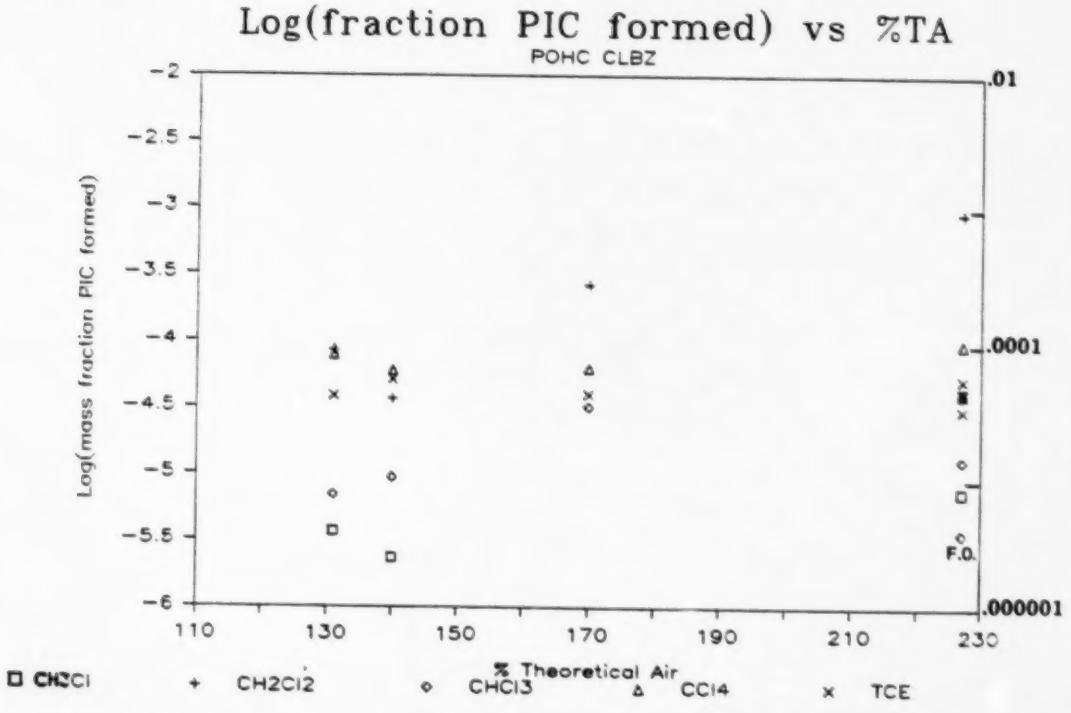

Figure 24. Mass Fraction of PIC Formed vs. %TA (from CLBZ).

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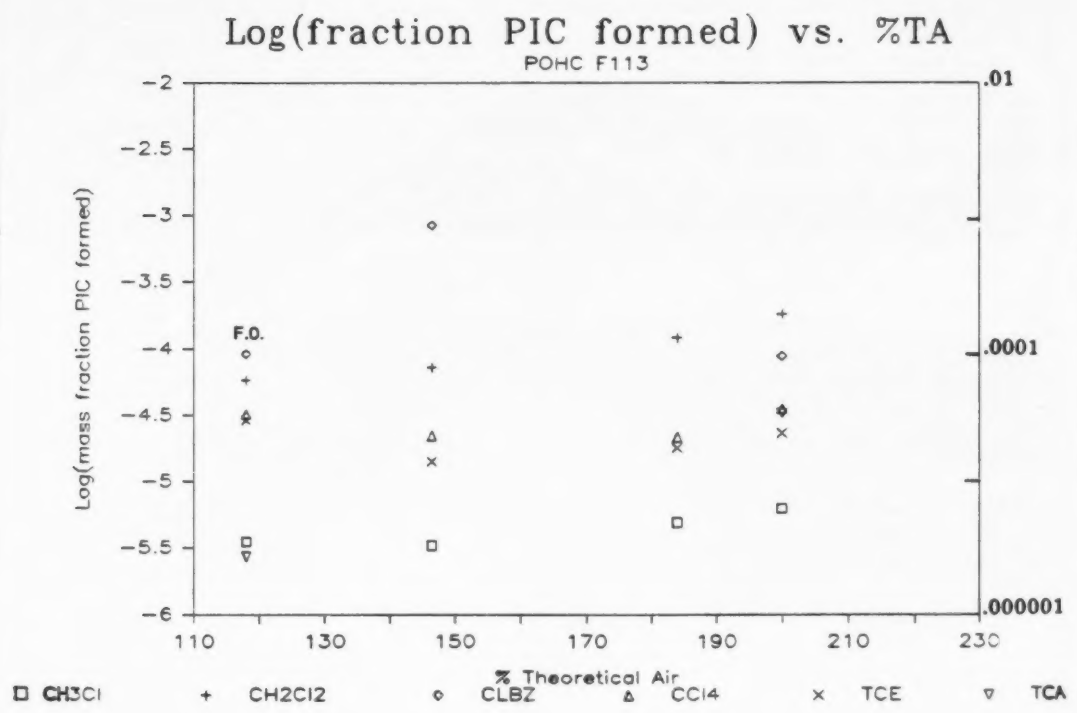

Figure 25. Mass Fraction of PIC Formed vs. %TA (from F113).

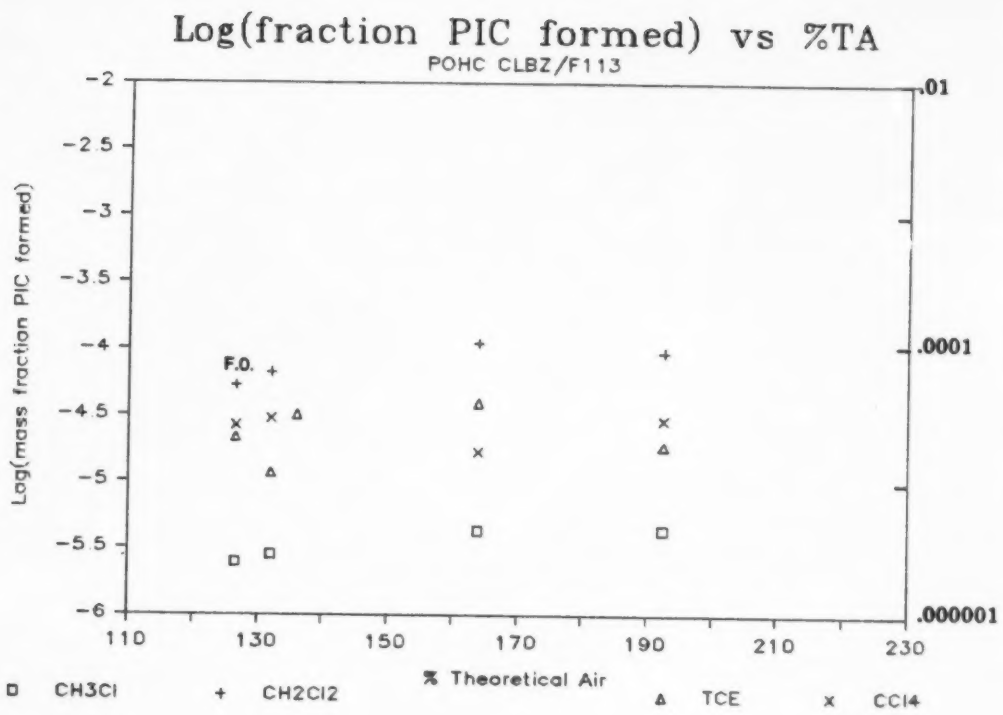

Figure 26. Mass Fraction of PIC Formed vs. %TA (from CLBZ/F113).

ting the particular distribution of PICs observed. It should be noted that the PICs detected in this study are among the most commonly occurring in full-scale boilers, kilns and incinerators (7).

Certain of the PICs commonly formed in the high excess air system, e.g., CLBZ, CCl_4 and TCE, are also often used as POHCs in trial burn tests. This may lead to problems in the interpretation of DE, and hence DRE. For example, since CLBZ seems to be readily formed by a recombination of benzene and chlorine atoms, it may turn out that there is a residual level of CLBZ exiting a boiler, below which, CLBZ levels cannot be reduced because of the amount of chlorine initially fed to the boiler. The amount of CLBZ formed might be relatively independent of the compound through which chlorine is introduced. Thus, if small amounts of CLBZ were "spiked" into the fuel/waste mixture, a poor DE could result, whereas when larger amounts of the CLBZ are introduced, an acceptable DE would be observed. This tendency to have lower DE at lower POHC concentrations has been commonly reported at the Annual EPA Research Symposia (8). A potential solution for this "POHC Selection" problem would be to select POHCs which are not likely to be reformed in the combustor, but which yield distinctive, difficult-to-destroy PICs. For example, 1,2,4-trichlorobenzene is not likely to be reformed, but can be expected to yield the likely PIC CLBZ which is also a highly-ranked compound (in terms of difficulty of incinerability) by several different incinerability ranking methods. Likewise, although Freon-113 has been reported to be fragile, its likely PICs Freon-11 and Freon-12 should be quite difficult to destroy and would give a characteristic signature since the level of fluorine fed in waste streams is typically less than chlorine. Studies of this type can be performed, for example, with the facilities available at EPA's Center Hill Facility in Cincinnati and are recommended as topics for future research.

Chloroform was one of the commonly detected PICs in this study. An earlier study by Kramlich et al. (1) reported that chloroform, burned in a mixture, was one of the most difficult-to-destroy compounds, and that it was not predicted to be so by any of the incinerability ranking scales examined except heat of combustion. The results of this study tend to support an alternative hypothesis, that chloroform was a PIC of the mixture of compounds and that the true DE of chloroform was not determined. Chloroform was not reported to be exceptionally difficult to destroy relative to CLBZ and CCl_4 in a recent pilot-scale study (4). The alternative of chloroform as a common PIC is consistent with field studies (7). Furthermore, the alternative hypothesis leads to a more consistent understanding of the relative success of the thermal stability incinerability ranking method as applied to field tests (9). A definitive test, firing chloroform alone, could and should be performed in the future.

Effect of Swirl Number and Nozzle Position on CO and POHC/Heptane DE

Swirl Number (S.N.) was varied from 0.62 to 2.39 while burning heptane. Those values represented the limits of flame stability at the optimum range of excess air, as defined by the CO minimum determined earlier. Over this range of S.N., gross changes in flame shape and stability were observed. At an S.N. of 0.62, the flame was long, smoky, and quite unstable, too

unstable to sample the exhaust under that condition. (The flame would extinguish spontaneously after adjusting S.N.) At S.N. = 0.86, the flame was observed to abruptly change shape, becoming more compact, brighter and not at all smoky in appearance. These flame characteristics were maintained up to a value S.N. = 1.13. In the range of S.N. from 1.13 to 2.39, the flame continually became brighter and even more compact. Above a value of about 2.4, the flame again became too unstable for continuous combustion.

Figures 27 through 30 present data on CO, fuel and POHC penetration as Swirl Number and nozzle position were varied. Although these data are preliminary in nature, they are suggestive of the potential importance of mixing effects, as reflected by changes in Swirl Number and nozzle position. For example, CO was observed to rise as Swirl Number was increased to a value near the stability limit of the flame (see Figure 27) even though nozzle position, fuel and air flowrates were held constant. Over a narrower range of S.N., before CO rose sharply, heptane penetration appeared to have decreased slightly with increasing S.N. (see Figure 28). It should be noted that the ordinate in Figure 28 has been greatly expanded in comparison to earlier graphs of logarithm of penetration. Also, a different analytical system (GC/MS) was employed to analyze the Tenax traps. Levels of heptane penetration at optimal %TA were low and the data are only suggestive of a possible effect of Swirl Number. Similarly, placement of the nozzle can affect the position of the fuel droplets in the secondary recirculation patterns set up by the swirling air. Thus, CO emission was observed to increase as the nozzle was progressively inserted farther into the TFR (see Figure 29). The corresponding effect one might expect to observe from the data obtained for fuel penetration was not so well defined (see Figure 30). An insufficient range of variation was observed to quantify effects and further study is needed. (A sampling system contamination problem curtailed further tests, but has now been resolved.) Nevertheless, the preliminary data indicate that "hardware" related operating parameters such as degree of turbulent mixing and nozzle/inlet air geometry can affect the efficient operation of a combustion device and presumably DE.

SUMMARY AND RECOMMENDATIONS

An initial assessment of the effects produced by varying several operating parameters of a pilot-scale turbulent flame reactor has been completed. Continuous sampling for conventional measures of incinerator performance such as CO, CO_2, O_2 and integrated sampling of POHC DE and PIC formation were performed under conditions of strong thermal quenching and variable levels of excess air. Preliminary studies of the effects of mixing resulting from changes in inlet air swirl and nozzle position were also carried out. A summary of the results obtained is presented below, as are recommendations for future research.

1. Over the range of excess air examined (120% < %TA < 230%), CO concentration and exhaust gas temperature were functions of the %TA in the TFR. The CO functional dependence was non-linear and non-monotonic, exhibiting a minimum at about 140% TA. CO production as a function of theoretical air appeared to be relatively insensitive to the particular POHC mixed with the fuel at the level tested, two mole percent. The

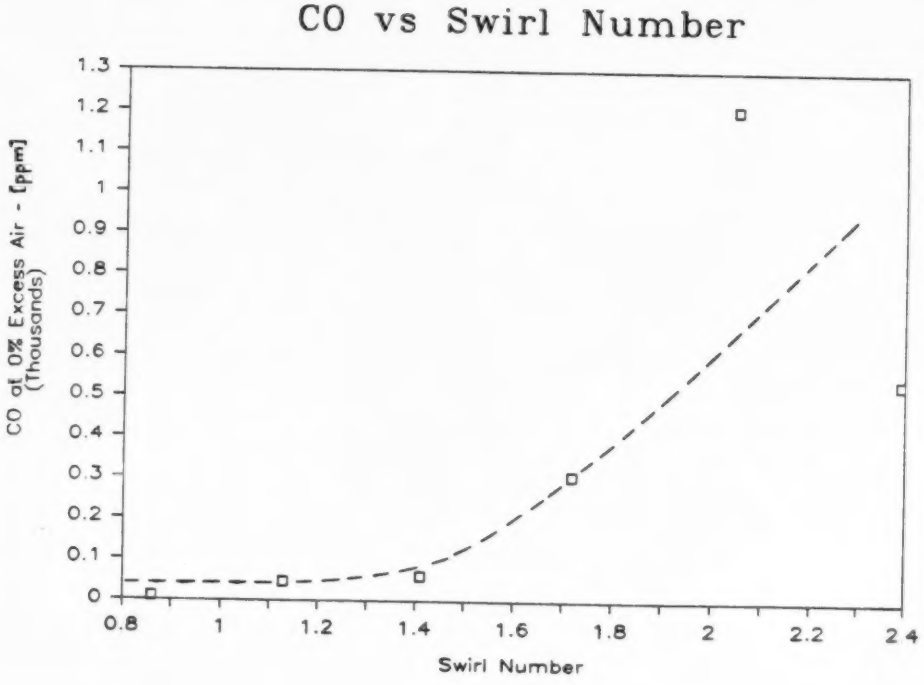

Figure 27. CO vs. Swirl Number (Heptane only).

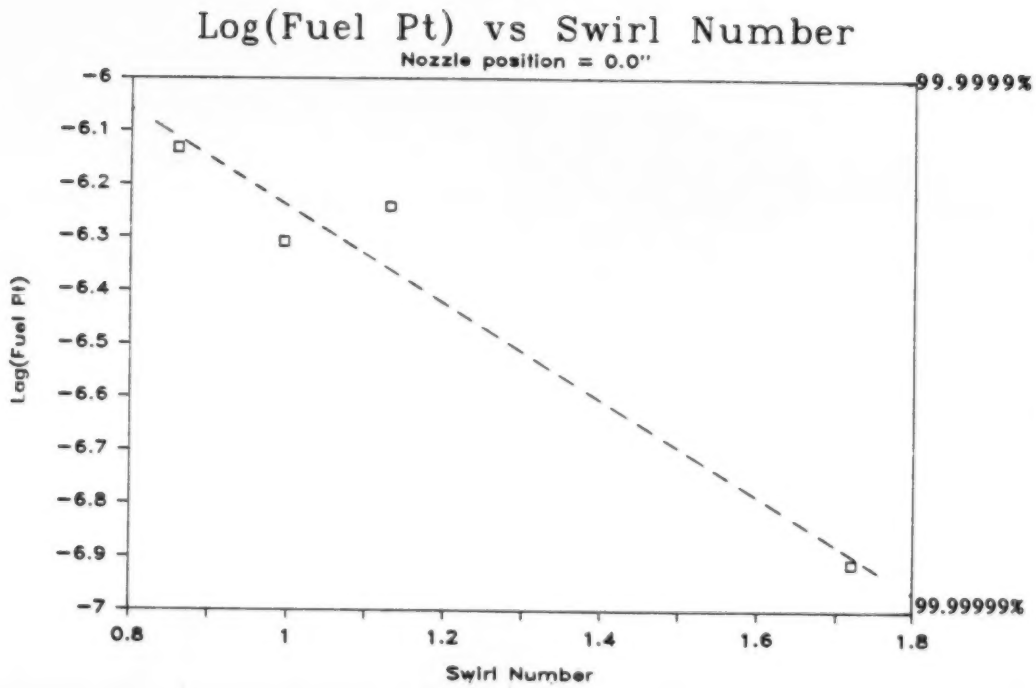

Figure 28. Fuel Penetration or DE vs. Swirl Numbers (Heptane only).

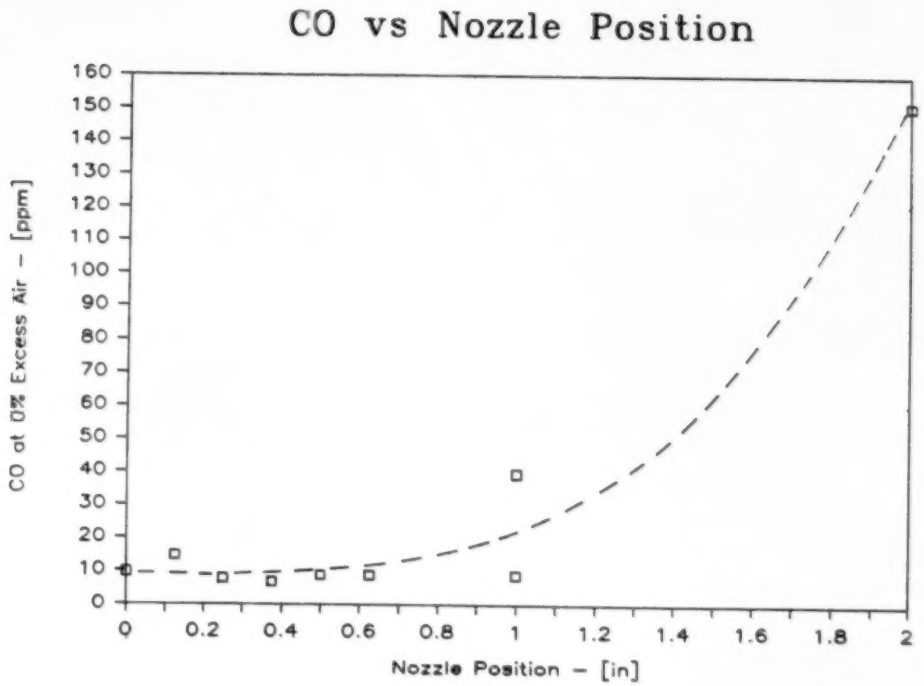

Figure 29. CO vs. Nozzle Position (Heptane only).

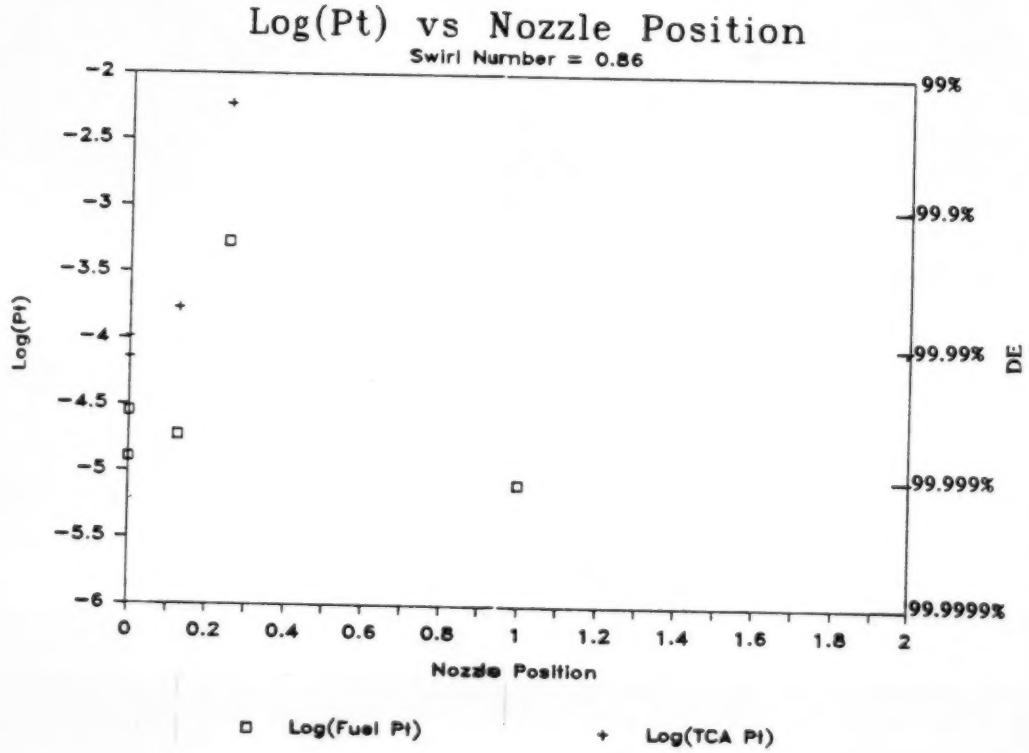

Figure 30. Fuel and POHC Penetration or DE vs. Nozzle Position (for Heptane-only and TCA-in-Heptane).

behavior of CO as a function of excess air could plausibly be attributed to poor mixing leading to locally fuel-rich pockets under conditions of low excess air, and to thermal quenching under conditions of high excess air. Exhaust temperature was a monotonically decreasing function of %TA over the range tested.

2. The existence of two limbs to the CO concentration versus %TA curve suggested correlating CO with POHC DE for one limb at a time. Adequate data were only available for the high excess air case. For the high excess air limb, POHC penetration appeared to increase as CO increased, but was dependent upon the POHC burned. Qualitative agreement with the thermal stability incinerability ranking scale was observed for the POHCs TCE, CLBZ, CCl_4 and TCA. Freon-113 exhibited anomalous behavior which possibly was related to an inability of the analytical method employed to distinguish Freon-113 from chloroform (a common PIC). The utility of CO as a continuous measure of POHC DE appears to be limited by the multiple-valued nature of the CO versus excess air curve as well as by dependence upon the POHC burned. Thus, it follows that the relationship between CO and DRE would be even more tenuous. Increase of CO emission did, however, precede or occur simultaneously with the increase in POHC penetration above about 130% to 140% of theoretical air. Therefore, CO concentration might still serve as a useful upper bound for purposes of incinerator permitting, but will likely be combustor dependent. Further research investigating the low excess air limb of the curve needs to be pursued.

3. The formation of PICs was observed to increase as a function of excess air under conditions of high excess air. The relative amounts of a given PIC formed was dependent upon the POHC burned, but numerous PICs were common to all POHCs tested. Thus it was observed that a recalcitrant PIC, TCE, could be formed from a relatively easily destroyed POHC, TCA. In fact, the PIC-to-POHC ratio was observed to be greater than unity in that instance, consistent with larger pilot-scale combustor tests under similar conditions of strong thermal quenching. The potential importance of this finding applied to boilers co-firing waste is evident.

4. The common occurrence of PICs (benzene, chloromethane, dichloromethane, chloroform, carbon tetrachloride and chlorobenzene) formed from the fuel and chlorinated POHCs may contribute to an understanding of the previously-found phenomena of increasing DE with increasing POHC concentration in the waste feed. POHCs which could also be formed as PICs would appear to be more difficult to destroy. The same phenomenon could be one possible explanation for the difficulties in using incinerability ranking scales to predict destruction efficiency. As a practical application of these findings, it is suggested that one select recalcitrant POHCs which are not likely to be formed as PICs but which also yield readily identifiable recalcitrant PICs as well. Further research to better understand the role of radical recombination in the formation of PICs should be pursued.

5. Hardware-related parameters such as degree of mixing produced by inlet air swirl and nozzle position were found to affect flame stability and CO emissions in preliminary testing. More comprehensive tests of the influence of such parameters on POHC DE should be carried out in the future.

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